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Application of DB-5ms gas chromatography column for the complete assignment of 2,3,7,8-substituted polychlorodibenzo-*p*-dioxins and polychlorodibenzofurans in samples from municipal waste incinerator emissions

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Abstract

The analysis of polychlorodibenzo-*p*-dioxins (PCDDs) and polychlorodibenzofurans (PCDFs) using four different gas chromatography (GC) columns (DB-5, DB-5ms, DB-DIOXIN and Cp-Sil 88) for the correct assignment and accurate determination of the 2,3,7,8-chloro-substituted isomers to attain the limit value of 0.1 ng I-TEF/Nm^3 (I-TEF=International Toxic Equivalent Factor) for the municipal waste incinerator (MWI) emissions is described. The DB-5ms GC column allows improvements in the analysis of PCDDs and PCDFs, especially for several toxic isomers which coelute with interfering compounds on DB-5, DB-DIOXIN or Cp-Sil 88 GC columns, such as 2,3,7,8-TCDF, 1,2,3,4,7,8-HxCDF, 1,2,3,7,8-PeCDD or 1,2,3,7,8,9-HxCDD. In fact, the results indicated that the column allows the correct assignment of fourteen toxic isomers. However, separation of 1,2,3,7,8-PeCDF or 2,3,4,7,8-PeCDF and 1,2,3,7,8,9-HxCDF shows interferences, which are critical.

Keywords: Polychlorodibenzo-*p*-dioxins; Polychlorodibenzofurans

1. Introduction

Nowadays, a number of countries such as Austria, Germany, the Netherlands and Sweden set limit values for polychlorodibenzo-*p*-dioxin (PCDD)/ polychlorodibenzofuran (PCDF) emissions into the air. Moreover, the European Community (EC) is preparing a Directive on hazardous waste incineration emissions in the air harmonizing the legal regulations of EC member countries, in which a dioxin emission limit value of 0.1 ng I-TEF/Nm^3 is proposed (94/67/CE). This obliges laboratories analyzing samples from municipal waste incinerator (MWI) emissions to provide a complete assignment of 2,3,7,8- substituted PCDD/PCDF in order to obtain an accurate determination of the most toxic isomers.

Generally, the analysis of PCDD/PCDF is carried out by high resolution gas chromatography coupled with high resolution mass spectrometry (HRGC–HRMS). HRMS at 10.000 resolution using positive electron impact (EI+) sources allows improved sensitivity in the lower femtogram range with the mass spectrometer operating in selected ion recording (SIR) mode. The separation of the seventeen toxic isomers from all non-toxic ones requires the

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use of HRGC. Many types of GC capillary columns with different compositions and polarities are available. Official organizations internationally recognized suggest several types of GC columns, for example: the US EPA [1] suggest the use of a DB-5 GC column, and DB-225 or SP 2330 (or equivalent) as a complementary column; Environment Canada [2] suggest the use of a DB-5 GC column and DB-DIOXIN as a complementary column, and the VDI [3] propose use of a DB-5, and a Cp-Sil 88 confirmation column or equivalent. Although a non-polar capillary column such as DB-5 allows the separation of the five groups with different degrees of chlorination [4], this column does not provide specific separation of all of the seventeen PCDD/PCDF toxic isomers. The analysis should be performed using a polar column such as DB-DIOXIN, Cp-Sil 88 or similar [5,6], in order to resolve some of the coelutions produced on the non-polar DB-5 GC column, although phenomenona such as coelution, adsorption and others which are difficult to understand, do not provide a total separation of the 2,3,7,8-chloro-substituted PCDD/PCDF [7].

In this paper, the results of samples analyzed from MWI emissions whose levels frequently are close to the limit of 0.1 ng I-TEF/Nm^3, with four different GC columns, are reported. Three of these are well-known: DB-5 and DB-DIOXIN and Cp-Sil 88, and the fourth GC column corresponds to the new DB-5ms phase, which is considered to be accurate, with characteristics similar to DB-5 but with a better accuracy for the quantification of 2,3,7,8 chloro-substituted PCDD/PCDF. Moreover, a high linear response for labelled and unlabelled toxic congeners is easily obtained and shows the capacity to achieve well-defined time windows for the homologous groups, except for the TCDF that elutes last (1,2,8,9-TCDF) which elutes after the first eluting PeCDF [8].

2. Experimental

2.1. Sampling

Stack gas samples were collected by sampling train (filter/condenser/adsorbent configuration), with XAD-2 (30 g) from Merck (Germany) as an adsorbent trap, operating isokinetically. Sampling process was controlled by spiking the filter with a recovery standard (^{37}Cl-2,3,7,8-TCDD) [9].

2.2. Soxhlet extraction

Samples were spiked with ^{13}C-labelled standards from Chemsyn Science Labs. (Lennexa, USA) before Soxhlet extraction. Organic pollutants were removed from XAD-2 and filtered using toluene as solvent for 48 h. Liquid–liquid extraction was performed to extract these PCDD/PCDFs from condensed water. Next, the extracts were mixed and concentrated prior to the clean-up process.

2.3. Clean-up method

The clean-up process was based on the use of a multilayer silica column (silica gel from Merck) and an alumina column (Basic Alumina 50–200 mesh, ICN Super I from ICN Biomedicals, Germany) at atmospheric pressure. Toluene, dichlormethane and *n*-hexane for organic trace analysis were purchased from Merck.

The multilayer silica column was composed of sequential layers of Na_2SO_4/SiO_2–H_2SO_4/SiO_2/SiO_2–$NaOH/SiO_2/SiO_2$–$AgNO_3$ and the alumina column required an activation at 300°C overnight. Both columns were coupled, and the PCDD/PCDFs were eluted in separate runs with 100 ml *n*-hexane and a 150 ml mixture of *n*-hexane–dichloromethane (1:1), the latter fraction containing the PCDD/PCDF. The clean-up process was controlled by HRGC with electron-capture detection (ECD) and for those cases which had interfering compounds, the analysis was performed with a carbon column (Carbopack C 80/100 at 18% mixed with Celite, both from Supelco, Bellefonte, PA, USA): 0.25 g of carbon were activated at 130°C overnight and prerinsed with different solvents in separate runs: 2.5 ml toluene, 1 ml toluene–dichloromethane–MeOH (15:4:1), 0.5 ml cyclohexane–dichloromethane (1:1). Then the column was kept at 130°C overnight. Next, the column was prerinsed with 2.5 ml of *n*-hexane and the sample extract was applied to the top column with 1.5 ml *n*-hexane. The interferences were eluted with 1.5 ml *n*-hexane and 2 ml dichlorometane–

cyclohexane (1:1). PCDD and PCDF were recovered by inverting the column with 30 ml toluene.

2.4. HRGC–ECD conditions

KONIK 3000 chromatograph (Konik, Barcelona, Sapin) with ECD (Tracor, Barcelona, Spain); DB-5 capillary column, 60 m×0.25 mm I.D. and 0.25 μm film thickness; injector: splitless; carrier: H_2 (v: 35 cm/s, T: 100°C); injector temperature at 275°C; temperature programme was: 140°C (0.7 min) to 200°C (1 min) at 20°C/min, then at 3°C/min to 300°C and held isothermally for 20 min at 300°C.

2.5. HRGC–HRMS conditions

Instrumental analysis was carried out by HRGC–HRMS. For high resolution, a mass spectrometer Autospec Ultima (Fisons Instruments, Manchester, UK) coupled to a GC 8000 series (Fisons Instruments, Milan, Italy) gas chromatograph was used.

For the HRMS an EI+ source at 250°C was used; the filament current was at 500 μA and electron energy at 37 eV; the resolution was 10.000 at 10% of valley on the analyzer mode SIR; the transfer line temperatures were 280°C and 50 ms of dwell time and 20 ms of interchannel time.

For the HRGC, four different fused-silica capillary columns were used: DB-5, DB-DIOXIN and DB5ms (J&W Scientific, CA, USA) and Cp-Sil 88 (Supelco) of 60 m×0.25 mm I.D. and 0.25 μm film thickness. Splitless injection, 1–2 μl, at 280°C (DB-5 and DB-5ms) and 260°C (DB-DIOXIN). Carrier gas: helium (v: 35 cm/s; T: 100°C). Programme temperature: DB-5 and DB-5ms: 140°C (1 min) to 200°C (1 min) at 20°C/min, then at 3°C/min to 300°C and held isothermally for 20 min at 300°C. DB-DIOXIN: 140°C (1 min) to 200°C (1 min) at 20°C/min then at 2°C/min to 200°C, then at 2°C/min to 270°C and held isothermally for 85 min at 270°C. Cp-Sil 88: 140°C (1 min) to 200°C (1 min) at 15°C/min then at 2°C/min to 200°C, then at 2°C/min to 240°C and held isothermally for 40 min at 240°C.

2.6. Identification and quantification

Identification of 2,3,7,8-chlorinated PCDD/PCDF was based on criteria reported by EPA (method 1613) [1], and quantification was carried out by isotopic dilution method using a mixture of a standard $^{13}C_{12}$-labelled (LCS 1613 from Chemsyn Science Labs.).

3. Results and discussion

The widespread use of the DB-5ms GC for the analysis of PCDD/PCDF from emissions of MWI indicates that this GC column enhances, in many cases, the separation of several toxic isomers compared with the separation observed on a DB-5 GC column. This can be observed in Fig. 1, which shows a comparison of a mixture of standards using DB-5ms, DB-5 and DB-DIOXIN GC columns. Fig. 2, also shows that 2,3,7,8-TCDD are well-resolved on a DB-5ms, which was reported by Fraisse et al. [8].

A large number of samples from MWI emissions, whose levels of PCDD/PCDF are close to the limit of 0.1 ng I-TEF/Nm^3, were analyzed. Frequently, a typical pattern on a DB-5ms GC column for a combustion process was observed. An example of this pattern is shown in Fig. 3(a,b), which indicates the DB-5ms behaviour in real samples from MWI emissions.

Table 1 shows the results of one sample from MWI emissions which were analyzed using the four different GC columns: DB-5, DB-5ms, DB-DIOXIN and Cp-Sil 88.

In general, all of 2,3,7,8-chloro-substituted PCDD are well resolved on the DB-5 GC column, except 1,2,3,7,8,9-HxCDD. The values obtained on the DB-5ms GC column are similar to those on the DB-5. Moreover, the results of 1,2,3,7,8,9-HxCDD obtained on a DB-5ms were the same, compared with the values found on the DB-DIOXIN or the Cp-Sil 88 GC columns, which are free of interferences in this compound.

On the other hand, one of most important advantages of the DB-5ms GC column was the improvement of the resolution of some 2,3,7,8-chloro-substituted PCDF, such as 2,3,7,8-TCDF or 1,2,3,4,7,8-HxCDF. Fig. 4 compares the DB-5, DB-5ms and the DB-DIOXIN GC columns, for the analysis of a real sample for the trace m/z 303.9016 (TCDF). The analysis indicates that the characterization of 2,3,7,8-TCDF is possible. However, the separation of this

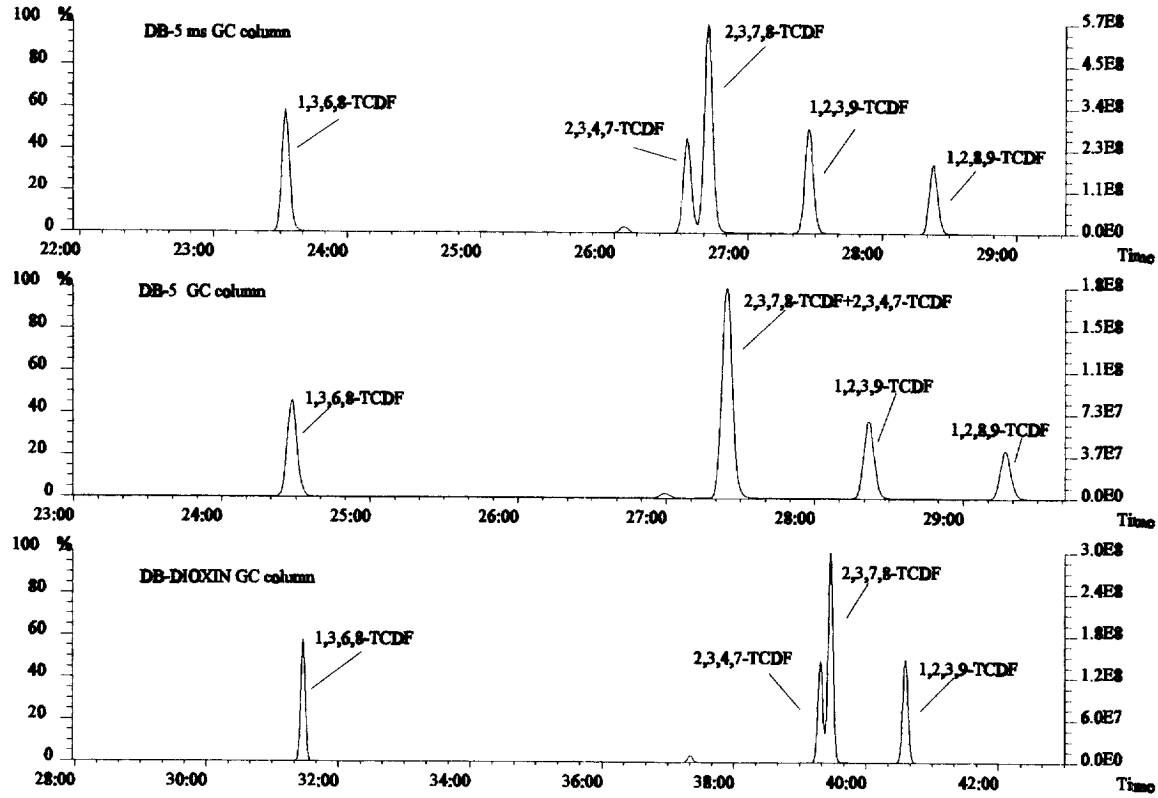

Fig. 1. Performance check column. Separation of 2,3,7,8-TCDF (trace *m/z* 303.9106) on the DB-5ms GC column.

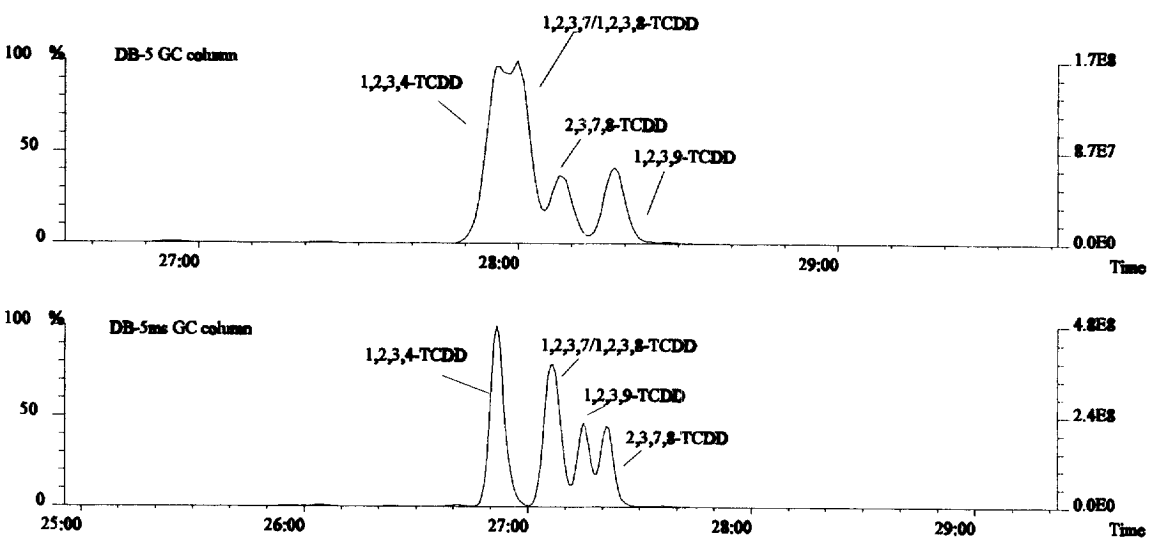

Fig. 2. Performance check column. Separation of 2,3,7,8-TCDD (trace *m/z* 319.8965) on the DB-5ms GC column.

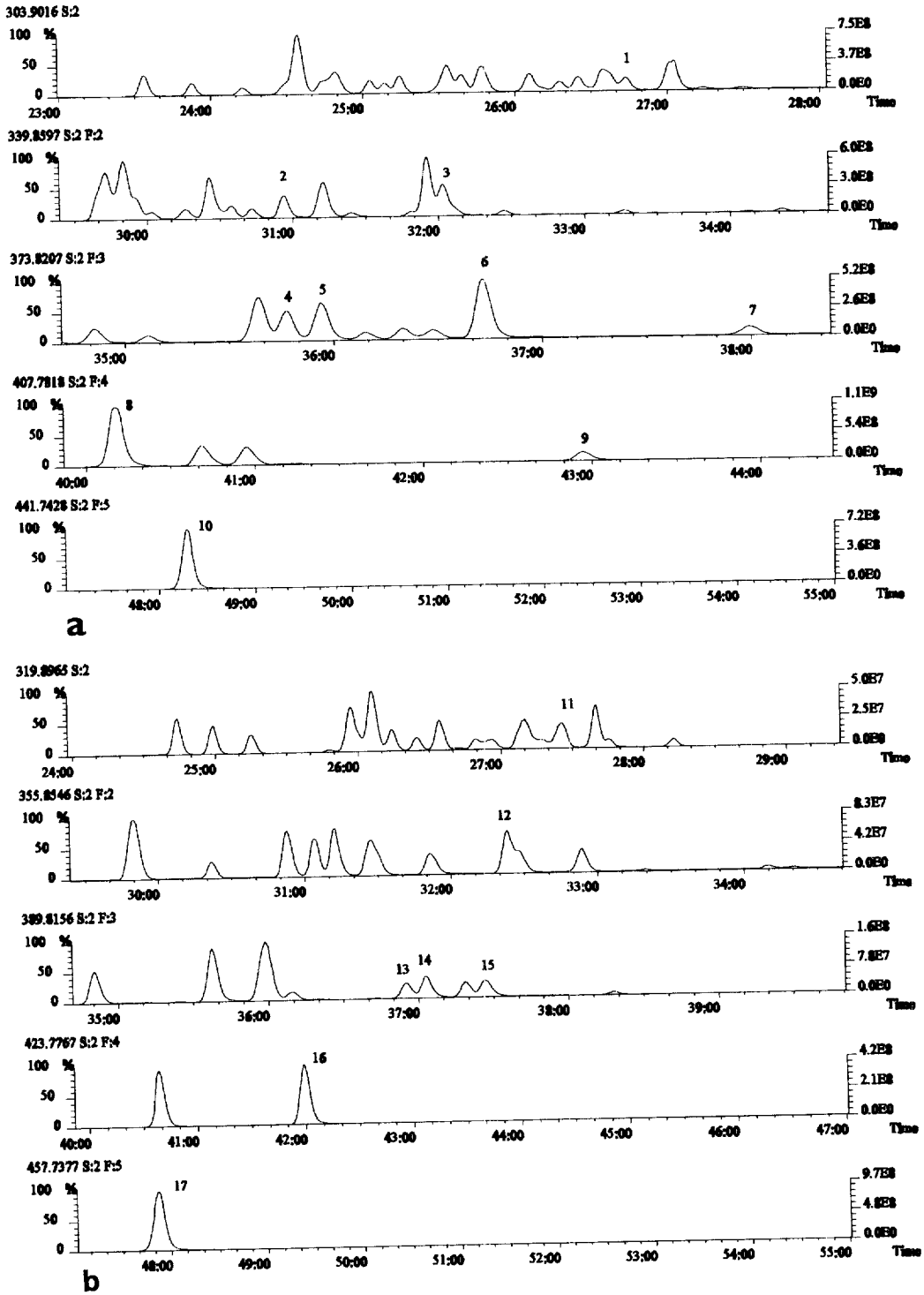

Fig. 3. (a) HRGC (DB-5ms)–HRMS (EI)-SIR chromatograms of the PCDF (tetra- through octa-chlorinated) of a MWI emission extract: (1) 2,3,7,8-TCDF; (2) 1,2,3,7,8-PeCDF; (3) 2,3,4,7,8-PeCDF; (4) 1,2,3,4,7,8-HxCDF; (5) 1,2,3,6,7,8-HxCDF; (6) 2,3,4,6,7,8-HxCDF; (7) 1,2,3,7,8,9-HxCDF; (8) 1,2,3,4,6,7,8-HpCDF; (9) 1,2,3,4,7,8,9-HpCDF; (10)-OCDF. (b) HRGC (DB-5ms)–HRMS (EI)-SIR chromatograms of the PCDD (tetra- through octa-chlorinated) of a MWI emission extract: (11) 2,3,7,8-TCDD; (12) 1,2,3,7,8-PeCDD; (13) 1,2,3,4,7,8-HxCDD; (14) 1,2,3,6,7,8-HxCDD; (15) 1,2,3,7,8,9-HxCDD; (16) 1,2,3,4,6,7,8-HpCDD; (17) OCDD.

Table 1
Levels of PCDD/PCDF from MWI emissions on DB-5, DB-DIOXIN, Cp Sil 88 and DB-5ms GC columns

PCDD/PCDF	DB-5ms (pg I-TEQ/Nm^3)	DB-5 (pg I-TEQ/Nm^3)	Cp Sil 88 (pg I-TEQ/Nm^3)	DB-DIOXIN (pg I-TEQ/Nm^3)
2,3,7,8-TCDD	0.47	0.46	0.42	0.43
1,2,3,7,8-PeCDD	1.50	1.73	1.81	3.63
1,2,3,4,7,8-HxCDD	0.62	0.70	0.72	0.66
1,2,3,6,7,8-HxCDD	1.59	1.63	1.89	1.87
1,2,3,7,8,9-HxCDD	1.32	3.06	1.42	1.36
1,2,3,4,6,7,8-HpCDD	1.46	1.43	1.66	1.42
OCDD	0.26	0.27	0.23	0.23
2,3,7,8-TCDF	0.30	5.64	0.26	0.24
1,2,3,7,8-PeCDF	0.50	1.76	1.22	0.40
2,3,4,7,8-PeCDF	18.38	16.15	11.52	18.68
1,2,3,4,7,8-HxCDF	4.22	16.31	6.98	4.28
1,2,3,6,7,8-HxCDF	7.09	6.90	8.67	6.28
2,3,4,6,7,8-HxCDF	26.65	25.34	2.81	22.14
1,2,3,7,8,9-HxCDF	11.60	1.63	1.83	1.32
1,2,3,4,6,7,8-HpCDF	6.36	6.44	7.96	6.55
1,2,3,4,7,8,9-HpCDF	2.17	2.19	2.61	2.23
OCDF	1.45	1.27	0.15	4.89

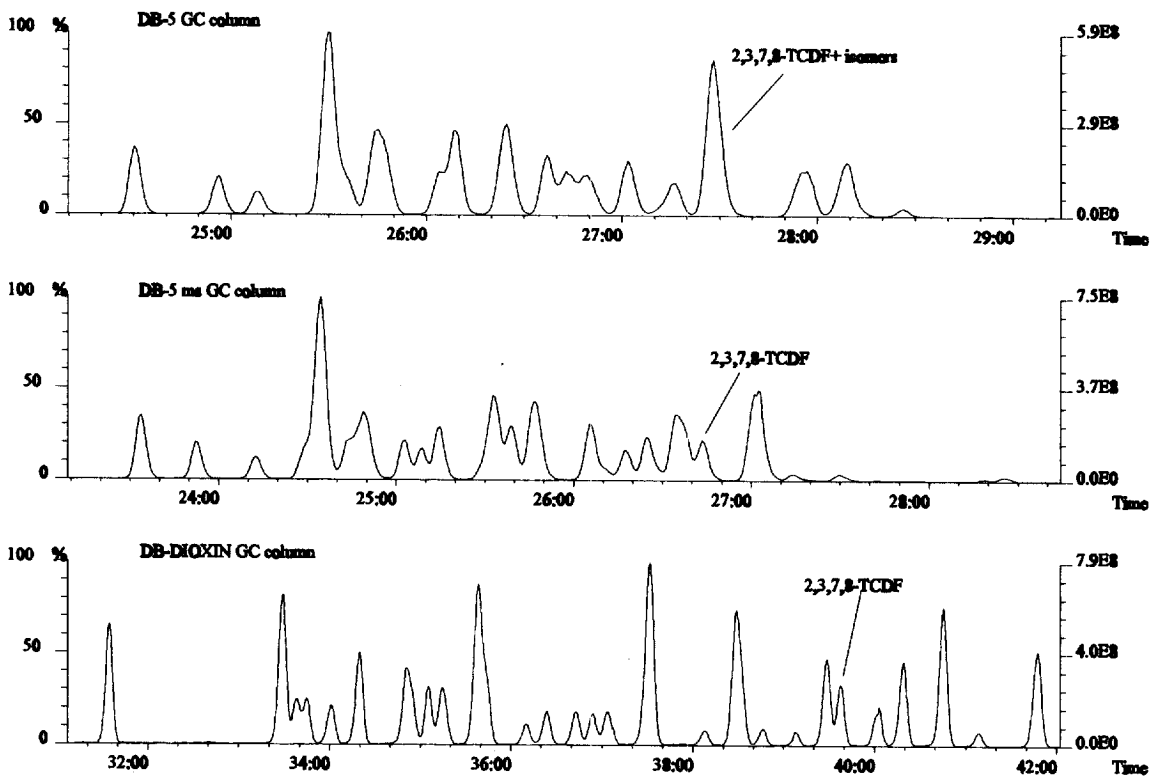

Fig. 4. HRGC–HRMS (EI)-SIR chromatogram of TCDF (m/z 303.9016) of a MWI emission extract on DB-5, DB-DIOXIN and DB-5ms GC columns.

isomer is poor owing to the low levels compared with the closest coeluting isomers, and with the characteristics of the DB-5ms column.

Special mention should be made of the 2,3,7,8-chloro-substituted PeCDF, which present coelutions with other non-toxic isomers on the DB-5 or DB-DIOXIN GC column. It was observed that 1,2,3,7,8-PeCDF was baseline separated on the DB-5ms GC column, as shown in Fig. 3a. However, the levels obtained were equally compared with the DB-5 or DB-DIOXIN, which indicates that the interferences are still present and given the low levels found in addition to the I-TEF of 0.05, this case is not a serious disadvantage.

So, the most important case studied was 2,3,4,7,8-PeCDF, due to the TEF of 0.5. Even though the levels obtained were lower than the values achieved on the DB-5 or DB-DIOXIN GC column (both with the coelutions with other non-toxic isomers), an incomplete separation was achieved for this congener on the DB-5ms, as shown in Fig. 5. In all cases studied, the comparative profile between the four GC columns indicates that the values obtained on the DB-5ms were higher than the values attained on the Cp-Sil 88 GC column, which can resolve this congener. Unfortunately, this indicates that DB-5ms does not provide an accurate separation of the 2,3,4,7,8-PeCDF.

The separation of 1,2,3,4,7,8-HxCDF from neighbouring isomers on the DB-5ms GC is also interesting. This isomer coelutes with 1,2,3,4,6,7-HxCDF on the DB-5 GC column, whereas on the DB-DIOXIN it provides a well-defined retention time, without the nearby isomers eluting in the vicinity, and quantification values obtained through DB-5ms and DB-DIOXIN were equal, which indicates that interferences present on the DB-5 could to be eliminated. Fig. 6 shows a specific separation of 1,2,3,4,7,8-HxCDF on the DB-5, DB-5ms and the DB-DIOXIN. Similar results were observed for the 1,2,3,6,7,8-HxCDF and 2,3,4,6,7,8-HxCDF. However, 1,2,3,7,8,9-HxCDF was baseline separated on the DB-5ms. As shown in Fig. 7, in all cases studied, the results obtained were higher than the results attained on the remaining columns. In fact, this is consistent with the comments of Fraisse et al. [8], who indicated that 1,2,3,7,8,9-HxCDF coelutes with 1,2,3,4,8,9-HxCDF.

Results also indicate that losses mainly due to adsorption process on a DB-DIOXIN GC column for

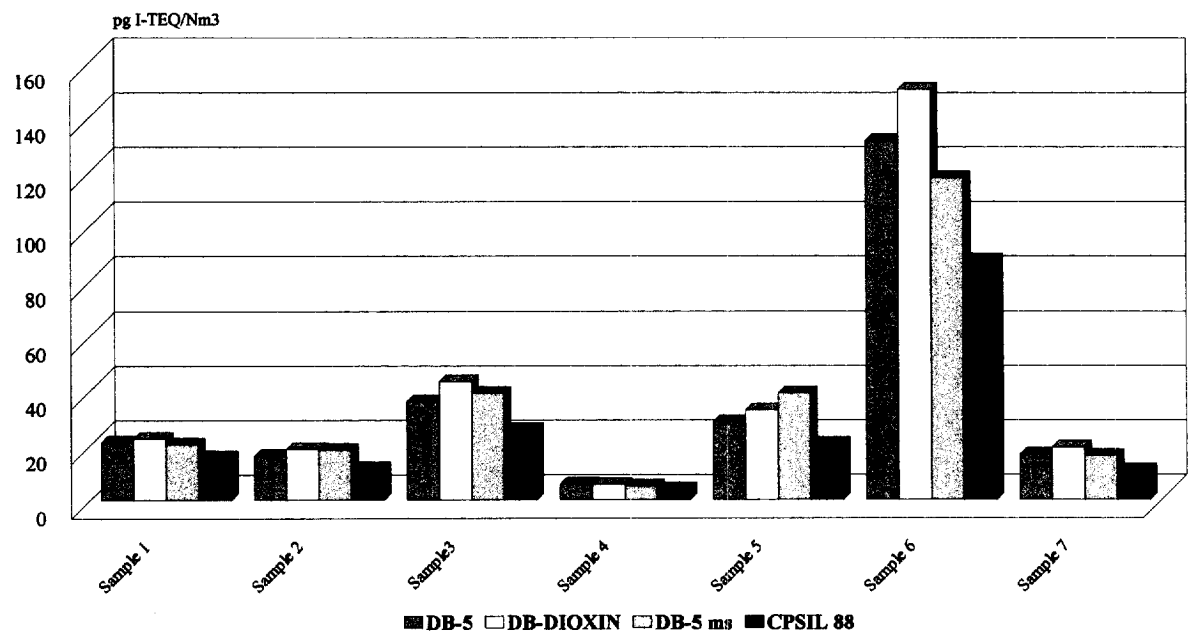

Fig. 5. Comparative profile: levels of 2,3,4,7,8-PeCDF on DB-5, Cp-Sil 88, DB-DIOXIN, DB-5ms GC columns.

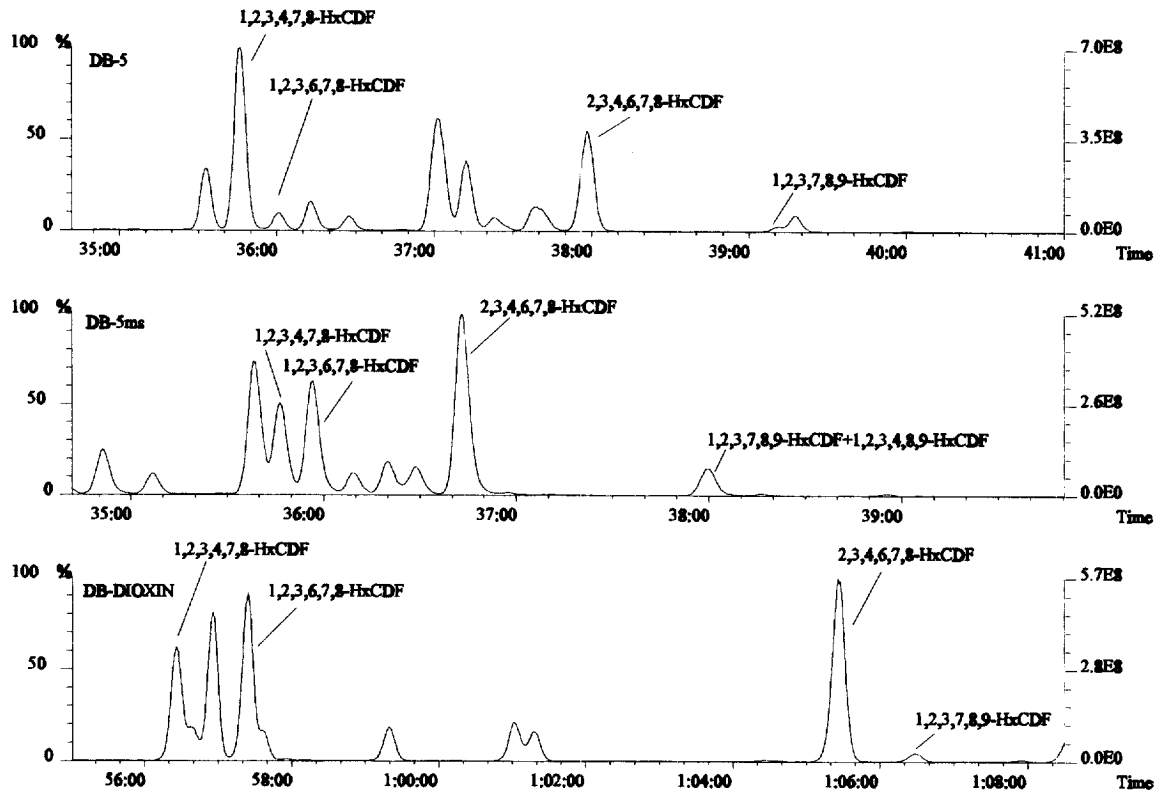

Fig. 6. HRGC–HRMS (EI)-SIR chromatogram of HxCDF (m/z 373.8207) of a MWI emission extract on DB-5, DB-DIOXIN and DB-5ms GC columns.

HpCDF, HpCDD, OCDF and OCDD determination [5], were not present on the DB-5ms GC column. Higher values measured for OCDF on the DB-DIOXIN column, could be accounted for on the basis of losses of $^{13}C_{12}$-OCDD, which was used as a quantification internal standard for this congener. For this reason, it would be advisable to include $^{13}C_{12}$-OCDF as an internal standard in the spiking solution for OCDF quantification. Finally, Table 2 shows an isomer specific separation of 2,3,7,8-substituted PCDD/PCDF on the DB-5ms GC column.

4. Conclusions

The DB-5ms GC column was studied for the correct assignment of 2,3,7,8-chloro-substituted PCDD/PCDF. Further improvements compared with a non-polar GC column such as DB-5 or a polar GC column such as DB-DIOXIN to asses MWI emissions for 0.1 ng I-TEF/Nm^3 compliance were obtained. The results indicated that the column allowed the correct assignment simultaneously of fourteen of the seventeen toxic isomers, while the other columns mentioned, DB-5, DB-DIOXIN and Cp-Sil 88 (dates reported by Bacher and Ballschmiter [5]) used independently could assign a maximum of between seven and nine toxic isomers. With the DB-5ms column 2,3,7,8-TCDF, 1,2,3,4,7,8-HxCDF and 1,2,3,7,8,9-HxCDD were solved simultaneously, while for the correct assignment the use of two of the above mentioned GC columns (DB-5, DB-DIOXIN or Cp-Sil 88) was necessary. However 1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDF and 1,2,3,7,8,9-HxCDF assignments constitute a disadvantage in using the

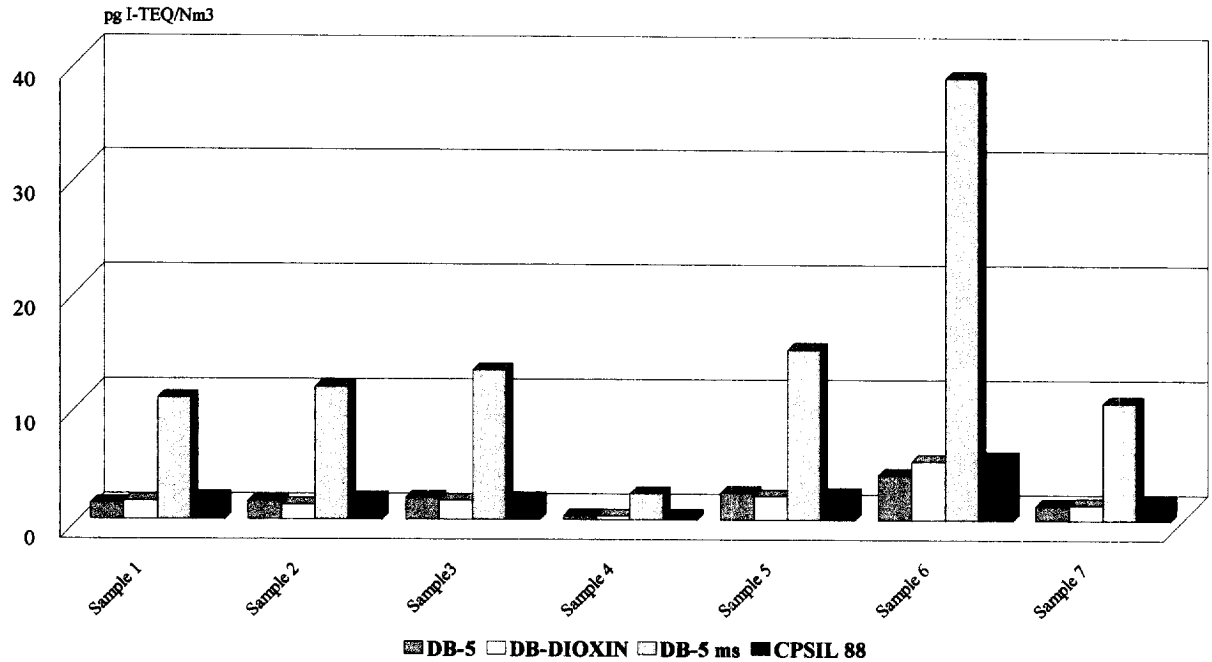

Fig. 7. Comparative profile: levels of 1,2,3,7,8,9-HxCDF on DB-5, Cp-Sil 88, DB-DIOXIN, DB-5ms GC columns.

Table 2
Isomer specific separation of 2,3,7,8-substituted PCDD/PCDF on the DB-5ms GC column

PCDD/PCDF	J&W DB-5ms
2,3,7,8-TCDD	++
1,2,3,7,8-PeCDD	++
1,2,3,4,7,8-HxCDD	++
1,2,3,6,7,8-HxCDD	++
1,2,3,7,8,9-HxCDD	++
1,2,3,4,6,7,8-HpCDD	++
OCDD	++
2,3,7,8-TCDF	++
1,2,3,7,8-PeCDF	+
2,3,4,7,8-PeCDF	−
1,2,3,4,7,8-HxCDF	++
1,2,3,6,7,8-HxCDF	++
2,3,4,6,7,8-HxCDF	++
1,2,3,7,8,9-HxCDF	−
1,2,3,4,6,7,8-HpCDF	++
1,2,3,4,7,8,9-HpCDF	++
OCDF	++

++: Baseline separated.
+: Partially separated.
−: Coelution with other congeners.

DB-5ms column. 1,2,3,7,8-PeCDF presents an interfering compound, although due its low levels and its I-TEF of 0.05 the disadvantage in using this column is minor. However, 2,3,4,7,8-PeCDF which is baseline separated on a Cp-Sil 88 GC column, present an interference which is critical due to its I-TEF of 0.5. On the other hand, 1,2,3,7,8,9-HxCDF coelutes with 1,2,3,4,8,9-HxCDF (date reported by Fraisse et al. [8]), which is a disadvantage when using the DB-5ms GC column. The use of the DB-5ms GC column definitely constitutes an improvement for the determination of PCDD/PCDF in samples from MWI emissions, even though a complementary column is still necessary for the full characterization of the three isomers.

Acknowledgments

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References

[1] EPA, Method 1613, Tetra- Through Octa-Chlorinated Dioxins and Furans by Isotopic Dilution HRGC–HRMS, Sept. 1994, Washington, DC.
[2] Environment Canada, Proposed Method for the Determination of PCDD and PCDF in Pulp and Paper Mill Effluents by Chemistry Division, River Road Environmental Technology Centre, Conservation and Protection, Environment Canada, 3rd Draft, June 1990.
[3] VDI Richtlinien, (3499) Emission Measurement. Determination of PCDD and PCDF, Düsseldorf, March 1993.
[4] J.J. Ryan, H.B.S. Conacher, L.G. Panopio, B.P.-Y. Lau, J.A. Hardy, J. Chromatogr. 541 (1991) 131–183.
[5] R. Bacher, K. Ballschmiter, Chromatographia 34 (1992) 137–142.
[6] T.O. Tiernan, J.H. Garret, J.G. Solch, L.A. Harden, R.M. Lautamo, R.R. Freeman, Chemosphere 20 (1990) 1371–1378.
[7] A.P.J.M. de Jong, A.K.D. Liem, R. Hoogerbrugge, J. Chromatogr. 643 (1993) 91–106.
[8] D. Fraisse, O. Paisse, L. Nguyen, M.F. Gonnord, Fresenius J. Anal. Chem. 348 (1994) 154–158.
[9] E. Abad, J. Caixach, J. Rivera, Chemosphere 35 (1997) 453–463.